



Electrochemical pyrolytic carbon resonators for mass sensing on electrodeposited polymers

Quang, Long Nguyen; Halder, Arnab; Rezaei, Babak; Larsen, Peter Emil; Sun, Yi; Boisen, Anja; Keller, Stephan Sylvest

Published in:
Micro and Nano Engineering

Link to article, DOI:
[10.1016/j.mne.2019.01.001](https://doi.org/10.1016/j.mne.2019.01.001)

Publication date:
2019

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

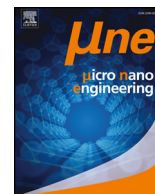
Citation (APA):
Quang, L. N., Halder, A., Rezaei, B., Larsen, P. E., Sun, Y., Boisen, A., & Keller, S. S. (2019). Electrochemical pyrolytic carbon resonators for mass sensing on electrodeposited polymers. *Micro and Nano Engineering*, 2, 64-69. <https://doi.org/10.1016/j.mne.2019.01.001>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



Research paper

Electrochemical pyrolytic carbon resonators for mass sensing on electrodeposited polymers

Long Nguyen Quang^{a,b}, Arnab Halder^c, Babak Rezaei^b, Peter Emil Larsen^{a,c}, Yi Sun^c, Anja Boisen^{a,c}, Stephan Sylvest Keller^{a,b,*}^a DNRF and Villum Fonden Center for Intelligent Drug Delivery and Sensing Using Microcontainers and Nanomechanics, IDUN, Denmark^b National Centre for Nano Fabrication and Characterization, DTU Nanolab, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark^c Department of Health Technology, DTU Health Tech, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

ARTICLE INFO

Keywords:

Electro deposition
MEMS resonators
Pyrolytic carbon
Mass sensing

ABSTRACT

In this work, we present the fabrication and characterization of a sensor combining electrochemistry with mass sensing. The sensor was realized using pyrolytic carbon, which is highly suitable as electrode material. A pyrolytic carbon resonator was embedded as working electrode in an electrochemical cell with a three-electrode configuration. Initial characterization using current-voltage (IV) measurements and cyclic voltammetry (CV) demonstrated that the pyrolytic carbon resonators were suitable as electrodes. The resonance frequency of the carbon resonators was measured to be 143.3 ± 3.4 kHz. The conductive properties of pyrolytic carbon were used to deposit Poly(3,4-ethylenedioxythiophene) (PEDOT) on the resonators by galvanostatic electropolymerization. The electrochemical carbon resonators were able to detect few nanograms of PEDOT added by electrochemical deposition.

1. Introduction

In the last four decades, research on methods and applications of electrochemistry combined with mass sensing techniques has dramatically increased [1,2]. With electrochemical methods, identification and quantification of analytes can be achieved with high accuracy which supports the selection of optimal conditions for scale-up processes in electrochemical synthesis [3] and scale-down for miniaturizing electrochemical assays on a chip [4,5]. Mass sensing techniques can support the study of electrochemical reactions. In parallel, electrochemical conversion of a sample can improve the response of a mass sensor in the detection of particular sample components [6,7]. The most popular combination of those two analysis techniques is the electrochemical quartz crystal microbalance (E-QCM). This tool has emerged as a powerful *in situ* technique to complement electrochemical experiments [8,9]. E-QCM combines a quartz crystal microbalance with a three-electrode electrochemical cell. Basically, one surface of the E-QCM crystal is employed as a working electrode while simultaneously extracting the mass changes by monitoring of the frequency of the QCM. E-QCM is a sensitive method to examine electrodeposition [10]. Furthermore, E-QCM has been used in many studies for obtaining detailed characterization of film deposition and dissolution [11,12] and for

studying the surface morphology and mass changes in thin films caused by chemical processes [8,13,14]. Similar to QCM, micromechanical resonators are powerful tools for mass sensing based on tracking changes of resonance frequency [15]. These devices have been widely investigated for detection of the mass of micro- and nanoparticles [16,17]. Similar to E-QCM, combining micromechanical sensors with electrochemical techniques is an promising approach to improve their performance and to explore new applications. Several studies have reported combined measurements, where microresonators also have been employed as a working electrode. For example, Au coated atomic force microscopy (AFM) microcantilevers have been used as working electrodes to measure the current-potential response (by cyclic voltammetry) and simultaneous bending characteristics in solutions of NaNO_3 and $\text{K}_3\text{Fe}(\text{CN})_6/\text{NaNO}_3$ [18]. Another example is silicon microcantilevers coated with Au on one side that have been used as working electrode to sense Pb and Cu using cyclic voltammetry [19,20]. This type of device was also used for controlling electrochemical deposition processes [21]. In the past five years, electrochemical cantilever (ECC) sensors have been developed by integrating a three electrode system together with cantilevers on a single chip [22,23]. These electrochemical cantilever sensors have shown promising potential for bio and chemical applications [23].

* Corresponding author.

E-mail address: Stephan.Keller@dtu.dk (S.S. Keller).<https://doi.org/10.1016/j.mne.2019.01.001>

Received 14 November 2018; Received in revised form 22 December 2018; Accepted 15 January 2019

2590-0072/ © 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Recently, carbon Micro Electro-Mechanical Systems (C-MEMS) has been introduced as a method to fabricate microstructures in pyrolytic carbon. Pyrolytic carbon is obtained in a pyrolysis process, where photoresist is pyrolyzed at high temperatures in an inert atmosphere [24,25]. The main advantage of using pyrolytic carbon as a resonator material is that its properties can be tailored by changing the pyrolysis parameters [26]. Additionally, pyrolytic carbon is electrically conductive which potentially can be used for actuation or readout. In fact, pyrolytic carbon has been used as an alternative to Au electrodes in electrochemical sensors for many applications [27–31].

In our previous work, we have introduced a new method for fabrication of pyrolytic carbon string resonators suitable for mass sensing [32]. Furthermore, the resonant behavior of different resonator designs has been investigated and the doubly-clamped beams with a length of 400 μm and a width of 30 μm provided the highest resonance frequency and quality factor.

Here, we investigated the potential application of pyrolytic carbon resonators as electrochemical mass sensors comparable to the E-QCM. For this purpose, we developed a process for the fabrication of a novel electrochemical pyrolytic carbon resonator integrated as working electrode in an on-chip three-electrode configuration. Initial characterization of electrical, electrochemical and mechanical properties of the sensor was performed. Next, the conductive polymer Poly(3,4-ethylenedioxythiophene) (PEDOT) was deposited on the pyrolytic carbon resonators by electrochemical deposition. Finally, by tracking the change of resonance frequency of the resonators, the total mass of deposited polymer was determined.

2. Materials and method

2.1. Fabrication of electrochemical pyrolytic carbon resonators

For the purpose of electrochemical deposition, a three-microelectrode configuration was designed on an electrode chip with overall dimensions of 1 cm \times 3 cm. In order to allow for integrated mass sensing, the working electrode (WE) was designed as suspended beam resonators. The WE and counter electrode (CE) consisted of pyrolytic carbon and the pseudo-reference electrode was Au. The design of the electrochemical carbon resonator chip for electrochemical deposition is shown in Fig. 1.

The fabrication process steps for electrochemical pyrolytic carbon resonators are illustrated in Fig. 2. First, 200 nm low stress Silicon Nitride (SiN) were deposited on N-type single side polished 4-inch wafers with a thickness of $525 \pm 25 \mu\text{m}$ using a Low Pressure Chemical Vapour Deposition (LPCVD) furnace (Fig. 2a-b). The SiN layer served as

insulating layer between the electrodes and the substrate. The temperature of the LPCVD furnace was set at 800 $^{\circ}\text{C}$, the deposition time was 40 min, ammonia (NH_3) gas flow was 50 sccm, Dichlorosilane (SiH_2Cl_2) gas flow was 200 sccm, and the pressure was 150 mTorr. Reactive ion etching (RIE) with photoresist as etch mask was used to open a window in the SiN layer defining the final length of 400 μm of the resonators (Fig. 2c). For this purpose, AZ5214E photoresist was spin coated by a Süss MicroTec Gamma 2 M spin coater to obtain a thickness of 2.2 μm . Then, UV exposure was done on a Süss MicroTec MA6/BA6 aligner with a dose of 200 mJ/cm^2 . The lithography step was concluded by developing the pattern using a Süss MicroTec Gamma 2 M developer for 60 s. The SiN layer was subsequently etched by dry etching in an Advanced Oxide Etcher (AOE) from STS. The parameters for SiN etching were: 700 W coil power, 100 W platen power, 5 sccm C_4F_8 flow, 174 He flow, 4 sccm H_2 flow. The etching process was performed at a pressure of 4 mTorr and a temperature of 0 $^{\circ}\text{C}$ for 5 min to open the window in the SiN layer. Stripping of the photoresist was performed in O_2 plasma at 400 sccm O_2 , 70 sccm N_2 , 1000 W for 15 min. Next, the SU-82005 device layer with a thickness of 7 μm was spin coated on top of the wafer using a Süss MicroTec RCD8 T spin coater for definition of the WE and CE patterns by UV photolithography (Fig. 2d). The spin speed was set at 1500 rpm for 30 s. Instead of a soft-bake, the solvent was evaporated at room temperature for 2 h. Subsequently, the SU-8 layer was exposed using a Süss MicroTec MA6/BA6 aligner with a dose of 200 mJ/cm^2 to pattern the WE and CE structures followed by a post-exposure-bake at 50 $^{\circ}\text{C}$ for 1 h on a programmable hotplate (Harry Gestigkeit GmbH, Germany). The development step was performed with PGMEA solution for a total of 4 min. After development, an additional hard-bake at 120 $^{\circ}\text{C}$ for 1 h was introduced. Next, isotropic Si dry etching was performed to release the SU-8 structures using a RIE with SF_6 as the reactive gas in a STS MESC Multiplex ICP Advanced Silicon Etcher (Fig. 2e). The parameters for isotropic etching were 1500 W coil power, 0 W platen power, etch temperature – 10 $^{\circ}\text{C}$ and etch time 6 min. After the isotropic etching step, the pyrolysis process was performed (Fig. 2f). A two-steps pyrolysis process was conducted in a PEO-604 furnace manufactured by ATV Technology with the parameters of 900 $^{\circ}\text{C}$ maximum temperature, fast ramping rate (30 $^{\circ}\text{C}/\text{min}$) and short dwell time (10 min) [32]. The Au pseudo-reference electrode and Au contact pads were deposited by e-beam evaporation through a shadow mask prepared using laser machining (Fig. 2g). After defining the Au contacts, an additional O_2 plasma step was performed for 5 min with 120 sccm of O_2 and a run power of 500 W to ensure that there was no short circuit between WE and CE. Finally, for passivating the contact leads, a 6 μm thick film of SU-82005 was spin coated and patterned with the same process as for the device layer described above (Fig. 2h).

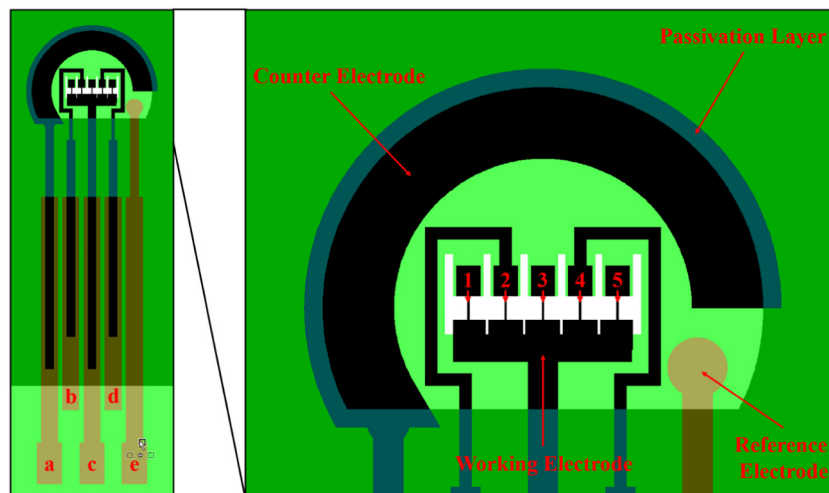


Fig. 1. Design of three electrode chip with working electrode with five integrated electrochemical pyrolytic carbon resonators for electrochemical deposition.

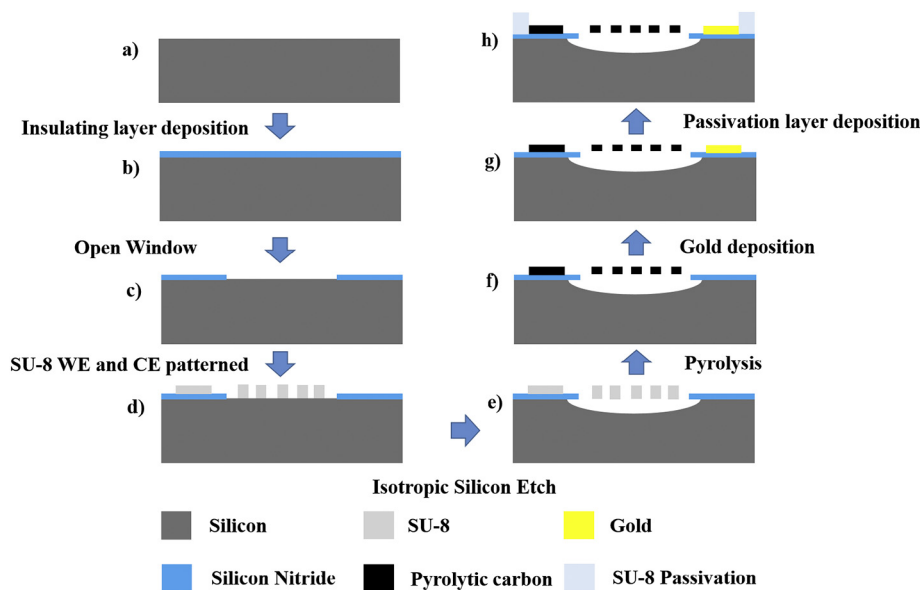


Fig. 2. Fabrication process of conductive carbon resonators for electrochemical deposition; a) Si wafer, b) SiN deposition, c) Photolithography and SiN dry etch to define resonators length, d) Patterning of SU-8 resonator WE and CE, e) isotropic Si etch, f) pyrolysis to obtain carbon resonator, g) Au electrode deposition and h) SU-8 passivation layer deposition.

The spin coating of the passivation layer did not affect the suspended carbon resonators and full coverage of the wafer was easily achieved despite the previous patterning steps.

2.2. Electrical and electrochemical characterization

In order to characterize the behavior of the electrochemical carbon resonators as electrodes, the electrical resistance of the devices was determined as well as the electrochemical performance.

The current-voltage characteristic curves (I-V curves) of pyrolytic carbon resonators were recorded to obtain the resistance of single resonators. A probe station and a Keithley 2450 source meter were used to apply a potential between the WE (Fig. 1, pad c) and one of the two auxiliary contacts (Fig. 1, pad b/d), and the I-V curves of pyrolytic carbon resonators 2 or 4 were recorded.

Electrochemical measurements were carried out using an Autolab PGSTAT128N potentiostat/galvanostat in combination with NOVA program version 2.1.3 (Metrohm Autolab B-V, Netherlands). Cyclic voltammetric (CV) experiments were carried out in a self-aligning magnetic clamping system including a static electrochemical cell (300 μL) with a solution of PBS containing 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at a scan rate of 50 mVs⁻¹ from -0.6 to 0.6 V [33]. The $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe was used as a model system to investigate the electrochemical behavior of the electrodes.

2.3. Electrochemical deposition

Electrochemical deposition was performed at room temperature ($23 \pm 2^\circ\text{C}$) using an Autolab System (EcoChemie, Netherlands) controlled by the NOVA 2.1.3 software. Galvanostatic electro polymerization of PEDOT was conducted using 0.01 M 3,4-Ethylenedioxythiophene (EDOT) monomer in 0.1 M KCl supporting electrolyte. Before electropolymerization, the EDOT monomer solution was deoxygenated using N_2 for 30 min. 50 μL of monomer solution were drop cast onto the electrode area and electro polymerization was performed at a current density of 0.2 mA/cm². Polymerization time was varied to deposit polymer films with different thicknesses on the WE surface.

2.4. Resonance frequency measurements

The resonant behavior of the pyrolytic carbon resonators before and after electrochemical deposition of polymer was measured with a MSA-500 laser-Doppler vibrometer. The measurement setup has been described elsewhere [32].

3. Results and discussion

3.1. Fabrication of electrochemical pyrolytic carbon resonators

Fig. 3a shows an image of an electrode chip with the electrochemical carbon resonators after completed fabrication. The working

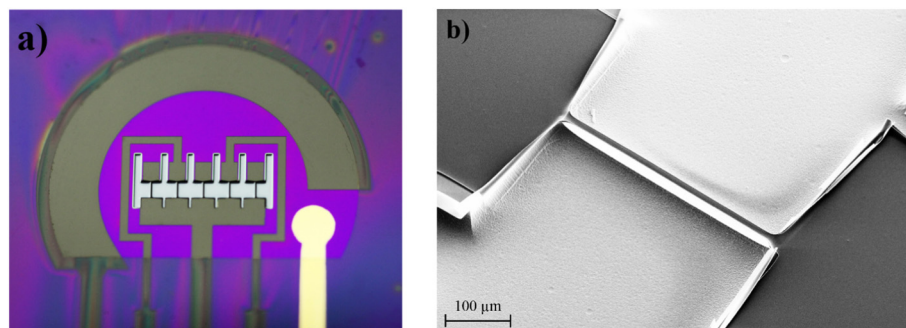


Fig. 3. Electrochemical pyrolytic carbon resonators: a) photo image of electrode area with 5 resonators as an integral part of the WE and b) SEM image of a single suspended resonator.

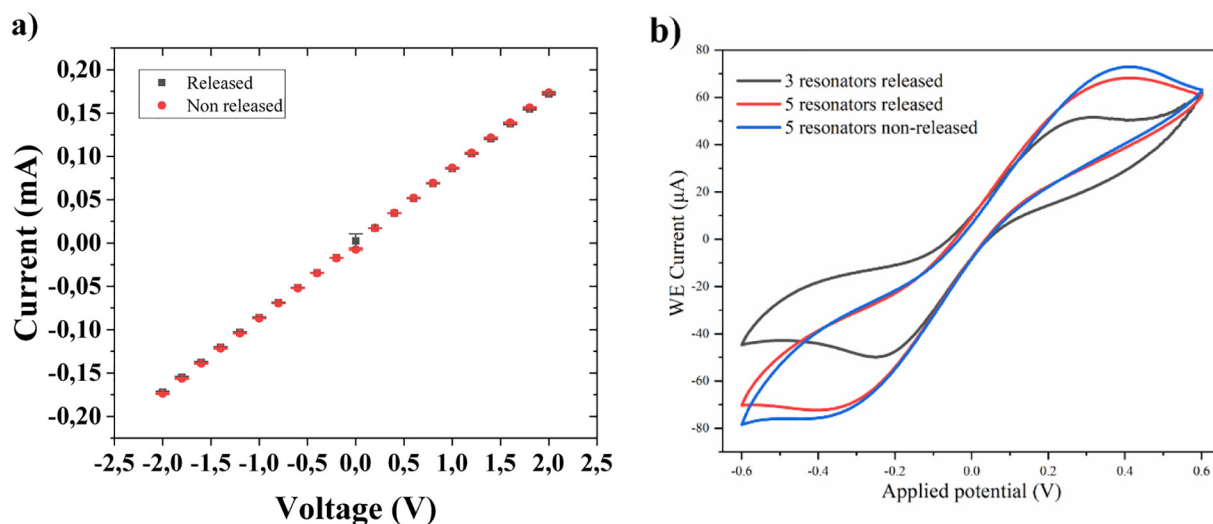


Fig. 4. a) I-V characteristics of single carbon resonators. Data is presented as mean \pm SD ($n = 15$) and b) Cyclic voltammetry with electrochemical pyrolytic carbon resonators.

electrode contains five pyrolytic carbon resonators, which can be used for mass sensing. Fig. 3b shows a close-up view of a single suspended carbon resonator with a final length of 400 μm and width of 20 μm . The thickness of the device layer changes during the fabrication process due to shrinkage during pyrolysis. Initially, the thickness of the SU-8 was 7 μm and after the pyrolysis process the carbon thickness was 717 nm. The final oxygen plasma step had no significant effect on the thickness of the device. A fabrication yield of 94% was achieved in this study.

3.2. Electrical and electrochemical characterization

For determining the electrical resistance of the resonators, current-voltage measurements were performed. Two different types of samples were prepared to identify eventual differences in resistivity of supported and suspended pyrolytic carbon electrodes: Resonators released from the substrate and non-released counterparts where the Si etching step was omitted. Fig. 4a shows the I-V characteristics of those two configurations displaying a perfectly identical ohmic behavior, which. Assuming that the resistance of the contact leads is negligible compared to the narrow resonator beam, the calculated resistance of a single carbon resonator was $11.52 \pm 0.07 \text{ k}\Omega$ (\pm STD, $n = 15$).

The electrochemical behavior of the carbon resonators was studied by cyclic voltammetry (CV) with the redox couple ferri-ferrocyanide $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$. This electrochemical evaluation can provide quantitative information about the electron transfer kinetics and the interaction between the electrode surface and electrolyte. Fig. 4b shows the cyclic voltammograms of electrode chips containing five released resonators and an identical pattern without release of the structures. It can be seen that there is an approximately identical peak-to-peak potential separation ΔE_p and a negligible difference in the redox peak currents for the released and non-released resonators. The results confirm that the etching step had no effect on the electrical and electrochemical properties of the resonator material.

According to the Randles-Sevcik equation, the redox peak current values in CVs depend on the electroactive surface area of the electrode A , the diffusion coefficient of the electrolyte in solution D , the number of electrons participating in the redox reaction n , the concentration of redox probe C and the voltage scan rate v [34]. Since C , D , n and v are all kept constant, the observed peak currents should be directly proportional to the electrode surface area A . To verify that the whole WE area was connected and contributing to the electrochemical signal, two resonators (#2 and #4 in Fig. 1) were manually removed. The observed significant drop in redox peak currents for this sample (Fig. 4b) is

mainly explained by a reduced electrode area due to the disconnection of the auxiliary contact leads (b and d in Fig. 1) from the rest of the WE. This indirectly confirms that the resonators were sufficiently conductive to connect all the electrode area and contribute to the electrochemical signals. The CV measurements demonstrated that the carbon resonators could be employed as a working electrode in different electrochemical reactions such as electro-polymerization.

3.3. Resonance frequency measurements

A vibrometer setup was used to extract the resonance frequency of the resonators. Fig. 5 shows an example of the frequency response in amplitude and phase of an electrochemical carbon resonator. The average resonance frequency was $143.3 \pm 3.4 \text{ kHz}$ (\pm STD, $n = 25$). Compared with our previous study [32], the resonance frequency of the pyrolytic carbon resonators was 30% lower. This can be explained by differences in resonator design (anchor point and frame) and in the fabrication process (insulating layer, etching process and thickness of the SU-8 layer). However, the resonators still behave as doubly clamped beams that are highly suitable for mass sensing.

3.4. Electrochemical deposition of PEDOT

The electrochemical carbon resonators showed promising

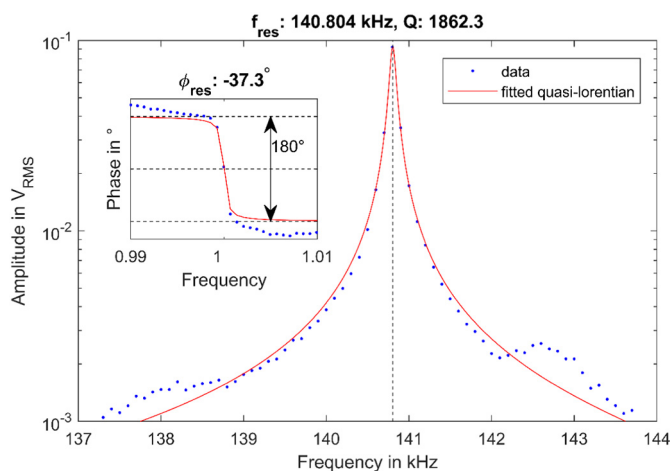


Fig. 5. Frequency response of carbon resonator in amplitude and in phase.

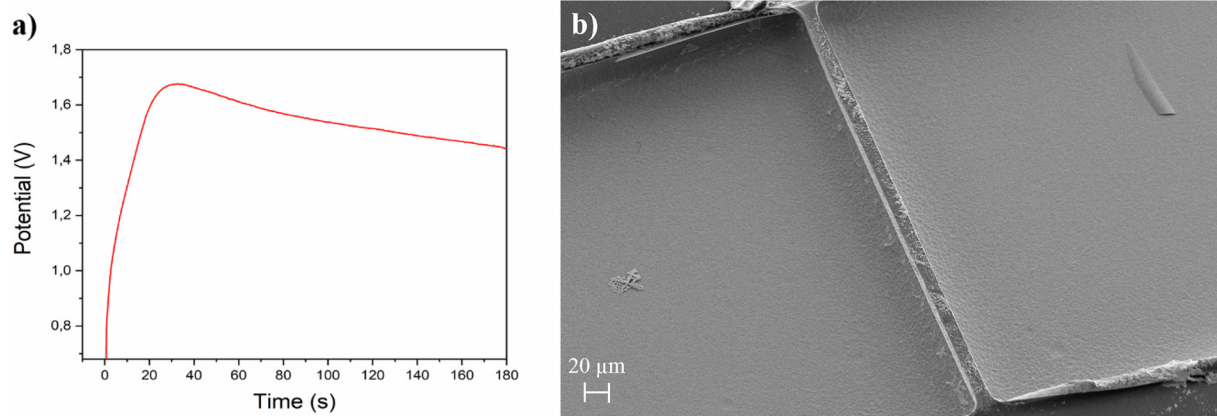


Fig. 6. a) Galvanostatic electropolymerization of PEDOT and b) SEM image of resonator after deposition.

performances as electrodes and resonators. In order to demonstrate the advantage of combining micromechanical mass sensing with electrochemistry, electrochemical deposition experiments were performed. The conductive polymer PEDOT was deposited on the resonators being part of the WE in the electrochemical cell. Fig. 6a shows the recorded electrodeposition profile of the process while Fig. 6b shows an SEM image of a resonator after a deposition time of 3 min. It was observed that PEDOT was deposited on all surfaces of the suspended pyrolytic carbon resonator.

Experiments with different times of electrochemical deposition were performed to compare the mass of the conductive polymer added on the resonators. For each condition, the resonance frequency of the resonators was measured before and after the deposition in order to calculate the added mass based on the equation [35]:

$$\Delta m = m_0 \left(\left(\frac{f_0}{f_0 - \Delta f} \right)^2 - 1 \right) \quad (1)$$

where Δm is the change in mass, Δf is the change of resonance frequency, m_0 and f_0 are the mass and resonance frequency of the resonator before deposition, respectively. Eq. (1) is based on the assumption that the effective stiffness of the resonator is constant before and after deposition and the deposited mass is distributed evenly over the length of the resonator. Fig. 7 summarizes the change in resonance frequency and the added mass for different times of electrochemical deposition. The results showed a linear increase of the resonance frequency shift and the added mass when the deposition time was increased. The added mass was estimated to approximately 8 ng for

15 min of deposition. The results demonstrate that the electrochemical carbon resonators can be a promising tool for characterization of the electrochemical deposition of polymers and other materials.

4. Conclusion

In conclusion, electrochemical pyrolytic carbon resonators were successfully designed, fabricated and characterized. With an optimized pyrolysis process, the pyrolytic carbon can be used as a conductive material for fabrication of doubly-clamped micromechanical beam resonators. The conductive carbon resonators were employed as the working electrode in an electrochemical cell with a three-electrode configuration. The initial electrical and electrochemical characterization showed that each carbon resonator had a resistance of approximately $11.52 \pm 0.07 \text{ k}\Omega$ and could be used as a working electrode. The resonance frequency of the carbon resonators was $143.3 \pm 3.4 \text{ kHz}$ which is suitable for mass sensing. Finally, the conductive polymer PEDOT was deposited by electrochemical deposition on the surface of the carbon resonators. By tracking the resonance frequency before and after electrochemical deposition, it was possible to calculate the mass of PEDOT. The deposited mass increased linearly with deposition time to approximately 8 nanograms after 15 min of deposition. The experiments demonstrate the advantage of a combination of mass sensing and electrochemistry. The electrochemical pyrolytic carbon resonators could potentially be used as a tool for monitoring the electrochemical or electrostatic deposition of a large number of different materials such as polymers, nanoparticles or charged biomolecules. Furthermore, bio

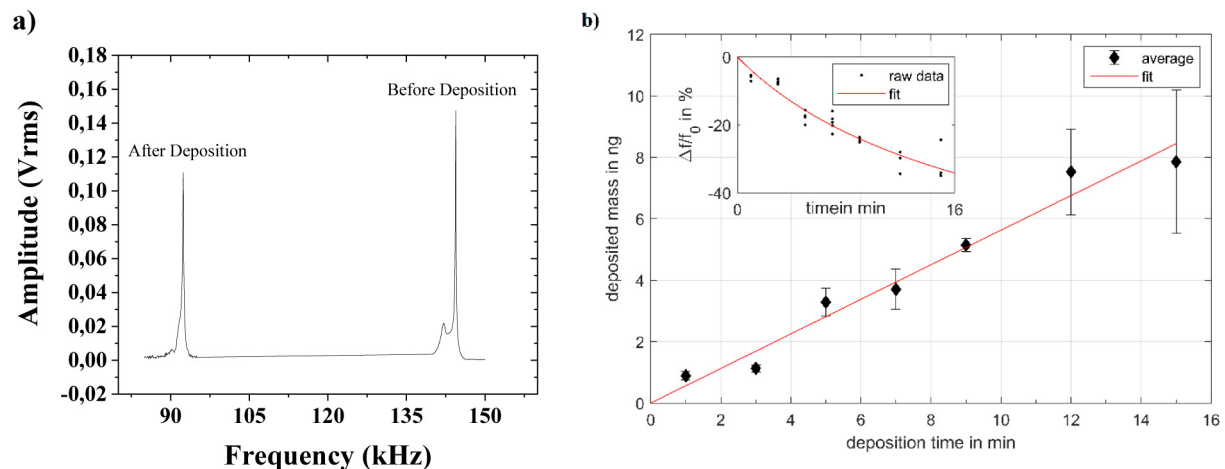


Fig. 7. a) Resonance frequency peak before and after 15 min electrochemical deposition of PEDOT and b) Change in resonance frequency (inset) and calculated added mass for different times of electrochemical deposition. Data is presented as mean \pm STD ($n = 3$).

functionalization and chemical modification of pyrolytic carbon electrodes in general could be characterized by mass sensing.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The research is funded by the Danish National Research Foundation (DNRF122) and Villum Fonden (Grant No. 9301). Center for Intelligent Drug delivery and Sensing Using Microcontainers and Nanomechanics (IDUN).

References

- [1] U. Karst, *Angew. Chem. Int. Ed.* 43 (2004) 2476.
- [2] F.M. Zhou, *Trends Anal. Chem.* 24 (2005) 218.
- [3] O. Hammerich, H. Lund (Eds.), *Organic Electrochemistry*, Fourth ed., Marcel Dekker, New York, NY, 2001.
- [4] V. Menges, O. Bagel, R. Ferrigno, H.H. Girault, A. Haider, A ceramic electrochemical microreactor for the methoxylatation of methyl-2-furoate with direct mass spectrometry coupling, *Lab Chip* 2 (2002) 39–44.
- [5] W.B. Zimmerman, *Electrochemical microfluidics*, *Chem. Eng. Sci.* 66 (2011) 1412–1425.
- [6] J.J. Van Berkel, J.M.E. Quirke, R.A. Tigani, A.S. Dilley, T.R. Covey, Derivatization for electrospray ionization mass spectrometry. 3. Electrochemically ionizable derivatives, *Anal. Chem.* 70 (1998) 1544–1554.
- [7] H. Hayen, U. Karst, Strategies for the liquid chromatographic-mass spectrometric analysis of non-polar compounds, *J. Chromatogr. A* 1000 (2003) 549–565.
- [8] D.A. Buttry, M.D. Ward, Measurement of interfacial processes at electrode surfaces with the electrochemical quartz crystal microbalance, *Chem. Rev.* 92 (1992) 1355–1379.
- [9] Chap. 7 M.D. in: Ward J. Rubinstein (Ed.), *Physical Electrochemistry*, Marcel Dekker, 1995, p. 293.
- [10] E. Gileadi, V. Tsionsky, Studies of electroplating using an EQCM. I. Copper and silver on gold, *J. Electrochem. Soc.* 147 (2000) 567–574.
- [11] S. Joiret, M. Keddam, X.R. Nóvoa, M.C. Pérez, C. Rangel, H. Takenouti, Use of EIS, ring-disk electrode, EQCM and Raman spectroscopy to study the film of oxides formed on iron in 1 M NaOH, *Cem. Concr. Compos.* 24 (2002) 7–15.
- [12] C. Olsson, D. Landolt, Passive films on stainless steels — chemistry, structure and growth, *Electrochim. Acta* 48 (2003) 1093–1104.
- [13] H.E. Hager, R.D. Ruedisueli, M.E. Buehler, The use of piezoelectric crystals as electrode substrates in iron corrosion studies: the real-time, in situ determination of dissolution and film formation reaction rates, *Corrosion* 42 (1986) 345–351.
- [14] C. Valero-Vidal, A. Igual-Munoz, C.-O.A. Olsson, S. Mischler, Adsorption of BSA on passivated CoCrMo PVD alloy: an EQCM and XPS investigation, *J. Electrochem. Soc.* 161 (2014) C294–C301.
- [15] A. Boisen, S. Dohn, S.S. Keller, S. Schmid, M. Tenje, Cantilever-like micro-mechanical sensors, *Rep. Prog. Phys.* 74 (3) (2011) 036101.
- [16] S. Schmid, M. Kurek, J. Adolphsen, A. Boisen, Detection of Airborne Nanoparticles with Mechanical Systems, (2013) (Spie Newsroom).
- [17] E. Sage, A. Brenac, T. Alava, R. Morel, C. Dupre, M.S. Hanay, M.L. Roukes, L. Duraffourg, C. Masselon, S. Hentz, Neutral particle mass spectrometry with nanomechanical systems, *Nat. Commun.* 6 (1) (2015) 6482.
- [18] F. Tian, J.H. Pei, D.L. Hedden, G.M. Brown, T. Thundat, Observation of the surface stress induced in microcantilevers by electrochemical redox processes, *Ultramicroscopy* 100 (3–4) (2004) 217–223.
- [19] A.F. Bange, G.M. Brown, L.R. Senesac, T. Thundat, Stripping voltammetry of Pb and Cu using a microcantilever electrode, *Surf. Sci.* 603 (21) (2009) L125–L127.
- [20] P.I. Oden, T. Thundat, R.J. Warmack, Electrochemical deposition induced stress measurements on a microcantilever investigated with cyclic voltammetry, *Scanning Microsc.* 12 (3) (1998) 449–454.
- [21] P. Prokaryn, P. Janus, J. Zajac, A. Sierakowski, K. Domanski, P. Grabiec, Gravimetric measurements with use of a cantilever for controlling of electrochemical deposition processes, *Proc. Spie Int. Soc. Opt. Eng.* 10161 (2016) 1016107.
- [22] L.M. Fischer, C. Pedersen, K. Elkjær, N.-N. Noeth, S. Dohn, A. Boisen, M. Tenje, Development of a microfabricated electrochemical-cantilever hybrid platform, *Sensors Actuators B Chem.* 157 (1) (2011) 321–327.
- [23] X. Quan, A. Heiskanen, S. Yi, A. Labuda, A. Wolff, J. Dulanto, A. Boisen, Development of electrochemical cantilever sensors for DNA applications, *E C S Trans.* 50 (12) (2013) 2077–2081.
- [24] C.L. Wang, M. Madou, From MEMS to NEMS with carbon, *Biosens. Bioelectron.* 20 (10) (2005) 2181–2187.
- [25] R. Martinez-Duarte, SU-8 photolithography as a toolbox for carbon MEMS, *Micromachines* 5 (3) (2014) 766–782.
- [26] J.A. Lee, S.W. Lee, K.-C. Lee, S.I. Park, S.S. Lee, J. Micromech. Microeng. 18 (2008) 035012.
- [27] S. Hemanth, C. Caviglia, S.S. Keller, Suspended 3D pyrolytic carbon microelectrodes for electrochemistry, *Carbon* 121 (2017) 226–234.
- [28] Y.M. Hassan, C. Caviglia, S. Hemanth, D. Mackenzie, T.S. Alstrøm, D.H. Petersen, S.S. Keller, High temperature SU-8 pyrolysis for fabrication of carbon electrodes, *J. Anal. Appl. Pyrolysis* 125 (2017) 91–99.
- [29] D. Sanchez-Molas, J. Cases-Utrera, P. Godignon, F. Javier del Campo, Mercury detection at microfabricated pyrolyzed photoresist film (PPF) disk electrodes, *Sensors Actuators B Chem.* 186 (2013) 293–299.
- [30] A. Singh, J. Jayaram, M. Madou, S. Akbar, Pyrolysis of negative photoresists to fabricate carbon structures for microelectromechanical systems and electrochemical applications, *J. Electrochem. Soc.* 149 (3) (2002) E78–E83.
- [31] D.J. Fischer, W.R. Vandaveer, R.J. Grigsby, S.M. Lunte, Pyrolyzed photoresist carbon electrodes for microchip electrophoresis with dual-electrode amperometric detection, *Electroanalysis* 17 (13) (2005) 1153–1159.
- [32] Long Nguyen Quang, Peter Emil Larsen, Anja Boisen, Stephan Sylvest Keller, Tailoring stress in pyrolytic carbon for fabrication of nanomechanical string resonators, *Carbon* 133 (July 2018) 358–368.
- [33] S. Hemanth, C. Caviglia, L. Amato, T.A. Anhøj, A. Heiskanen, J. Emnéus, S.S. Keller, Pyrolytic 3D carbon microelectrodes for electrochemistry, *ECS Trans.* 72 (1) (2016) 117–124.
- [34] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, 2001.
- [35] S. Schmid, L.G. Villanueva, M.L. Roukes, *Fundamentals of Nanomechanical Resonators. Fundamentals of Nanomechanical Resonators*, (2016), pp. 1–175.